Eutectic solidification of polymer solutions

Smith, Paul

CHAPTER 7

SUMMARIZING CONCLUSIONS

The results of this study on eutectics in polymeric systems, involving both the requirements for their occurrence and the mechanism of the eutectic solidification reaction, will be summarized in this chapter. In addition an attempt is made to indicate possible fields of application of this particular solidification process of polymer/diluent(s) alloys.

The equilibrium theory of Flory and Huggins of melting point depression in polymeric systems predicts well defined eutectic points in both binary polymer/diluent and ternary polymer/diluent/diluent systems, if the melting point of the constituents do not differ substantially. More specifically, in mixtures containing the apolar polyethylene, allowing no specific interactions, an experimentally observable eutectic point occurs in a quasi binary polymer/diluent system if the melting point of the diluent exceeds 110^{o}C. It has been shown that to observe a eutectic point in a quasi ternary polyethylene/diluent/diluent system also the binary eutectic temperature of the diluents system should exceed 110^{o}C (Chapter 4).

The theoretically derived requirements for the occurrence of eutectics have been verified experimentally by the determination of phase diagrams of a number of polyethylene/and polypropylene/diluent(s) systems (Chapter 5). Due to the fact that crystallizable polymers generally produce metastable semi-crystalline solids, the eutectic points in macromolecular systems have a metastable character, and consequently are dependent on experimental circumstances. Nevertheless, the eutectic temperature and composition could be described very well by the simplified relations derived by Flory for melting point depression in macromolecular systems, when the influence of the amorphous fraction and crystalline defects on the melting point and heat of melting of the polymer was taken into account

by substitution of the experimental value for these parameters.

The mechanism of the eutectic solidification of polymer/diluent(s) systems has been investigated by studying the influence of the solidification parameters in the simultaneous crystallization process on the microstructures produced. As outlined in Chapter 2 and 3, these parameters are the rate of solidification (in the unidirectional solidification experiments), the undercooling and the faceted or nonfaceted behaviour of the diluents. Investigations were performed using light- and scanning electron microscopy (Chapter 6). It was found that uncoupled, nucleation controlled, growth of the constituents occurred at rates of solidification lower than about 3 mm/hr in a temperature gradient of $3^{o}C/mm$. The eutectic microstructures produced consisted of randomly mixed crystals of the constituent phases. At growth rates exceeding 3 mm/hr the nature of the simultaneous solidification of macromolecules and diluent molecules depended on the faceted or nonfaceted habit of the diluent. Weakly coupled eutectic growth of the components was observed in systems containing a faceted growing diluent, such as 1,2,4,5-tetrachlorobenzene. Complex regular microstructures were produced with a characteristic dimension of about 0.7 μm. In the solidification of macromolecular systems comprising a nonfaceted growing diluent, such as pentaerythrityltetrabromide or bornylchloride, the eutectic reaction proceeded in a strongly coupled manner. A lamellar microstructure was produced by the polyethylene/bornylchloride eutectic. The system isotactic polypropylene/pentaerythrityltetrabromide formed a rod eutectic microstructure, in which diluent rods were dispersed in a polymer matrix. In both microstructures the mean characteristic dimension (λ) ranged from 0.1-1 μm, and depended on the growth rate (R) according to the relation $\lambda^2.R$ = constant. The value of the constant amounted to about 10^{-9} mm^3/s. This value is in agreement with the one calculated with the theory of small molecular and atomic eutectic growth of Jackson and Hunt, using the crystallization point curves of the metastable polymer crystals.

Despite the complexity of the simultaneous crystallization in concentrated polymeric systems due to the entanglements, the polymer ex-

hibited a nonfaceting character at rates of solidification exceeding 3 mm/hr, indicating that in this solidification process the chain segments should be considered as the crystallizing entities.

Obviously, a discussion on the possible applications of eutectic solidification of polymer solutions cannot be a complete topic. The present study was undertaken to explore theoretical and experimental requirements for the occurrence of eutectics in polymeric systems and, moreover, to gain some understanding of the very nature and the underlying mechanism of the simultaneous crystallization of macro- and small molecular species. For this purpose model systems have been selected, in which no specific features were expected to occur obscuring the eutectic solidification process, rather than composing polymeric systems from commercial polymers and well-choosen, applied, additives. Nevertheless, our present understanding of eutectic solidification of polymer solutions allows us to indicate possible interesting fields of application of this process.

The applications of eutectic solidification of polymer solutions may be divided in the two areas to be discussed hereafter. This is first of all, the production of polymer composite materials, referring to heterogeneous materials consisting of two or more solid phases, with characteristic dimensions in the range from 0.01-100 μm. Secondly eutectic solidification of polymer solutions may be applied in producing porous macromolecular structures, by removal of the diluents from the solidified eutectics.

In view of applications, the most important feature of eutectic solidification is the characteristic dimension of the microstructures produced (0.1-1 μm), its dependence on the growth rate (roughly $\lambda^2.R$ = constant) and the possibility to alignment of the constituent phases in temperature gradients. The phase periodicity in the micron range allows the properties of the composite eutectic to differ essentially from those of the constituents. Crystals having a transverse diameter in the range of 0.1-10 μm, and a length exceeding the cross section by orders of magnitude, are generally referred to as whiskers. These whisker-like crystals frequently exhibit unique mechanical properties and are therefore much applied in material reinforcement. The problem

in the production of these reinforced materials is the homogeneous dispersion of the difficult maintenable whiskers, without distroying them. Clearly the eutectic solidification process gives an answer to this dispersion problem. Quenching of the eutectic liquid produced random distribution of the solids involved, giving rise to isotropic properties. Directional solidification may yield well-aligned structures with anisotropic properties. From the present study it follows that alignment can only be obtained in polymeric films or thin fibers (see Chapter 6), rather than in bulk materials. The final properties of the solidified eutectics naturally largely depend on those of the constituents, i.e. the polymer and the additive(s), including antioxidants, u.v. stabilizers, dyes, nucleating agents, tackifiers, antistatics, etc. Special attention should be paid to eutectics of a polymer and a polymerizable monomer giving possibility for producing polymer/polymer composites.

The second field of application of polymeric eutectics involves porous macromolecular materials. By removal of the diluents from the solidified eutectics porous polymeric structures can be produced, in which the pore size depends uniquely on the rate of solidification, roughly according to the $\lambda^2.R$ = constant relation (see Chapters 3, 6). Consequently, eutectic solidification of polymeric systems provides a tool in the preparation of porous materials in which the pore diameter can be governed to a large extent. As demonstrated in the previous chapter for systems containing low molecular weight polymeric species, eutectic solidification produces regular structures with continuous pores, rather than in high molecular polymer systems. The loss in mechanical properties due to applying these low molecular weight polymer species may be reduced by cross-linking the macromolecules after the solidification reaction.

Especially in the preparation of polymeric membranes, hollow fibers, etc. eutectic solidification may be of importance, since in manufacturing these species high temperature gradients can be applied, which are known to promote regular eutectic growth.